

Influence of Structure and Counterions on Physicochemical Properties of Linear Alkylbenzene Sulfonates

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The effects of different inorganic and organic counterions on the physicochemical behavior of three commercial linear alkylbenzene sulfonates (LAS) have been studied. It has been found that the counterion hydration radius of the corresponding commercial linear alkylbenzene sulfonates has great influence on solubility, viscosity, surface tension and critical micelle concentration (CMC). The counterion has no influence on the detergency performance of the finished formulation. The alkyl chain length and the presence of tetralines have an important influence on solubility, viscosity and surface tension.

KEY WORDS: Alkylbenzene, counterion, detergency, solubility, sulfonate, viscosity.

The most frequently used anionic surfactant, linear alkylbenzene sulfonate or (LAS), is produced as a salt by neutralizing it with an inorganic cation or with an organic cation as the counterion. The nature of this counterion has an important influence on the physicochemical properties of the final sulfonate (1,2). The following will be considered in this study: solubility, viscosity, surface tension, critical micelle concentration (CMC) and detergency performance.

The neutralizing ions used were the inorganics: Li^+ , Na^+ , K^+ and NH_4^+ or the organics: monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA).

This study was carried out using three commercial alkylbenzene samples whose composition is indicated in Table 1. They were sulfonated in a laboratory pilot plant unit with SO_3 gas using a SO_3 /linear alkylbenzene (LAB) molar ratio of 1.07, a SO_3/N_2 weight ratio of 4.34% and a temperature of 45°C.

TABLE 1

Analysis of Linear Alkylbenzenes Used (wt%)

	Sample 1	Sample 2	Sample 3
Phenyl C9	0.92	0.77	0.17
Phenyl C10	15.84	7.93	9.97
Phenyl C11	41.29	32.54	26.59
Phenyl C12	36.74	29.86	28.35
Phenyl C13	5.21	26.48	17.54
Phenyl C14	—	1.96	1.20
Tetralines	—	0.46	16.18
Molecular weight	236.3	242.3	240.3

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Samples 1 and 2 were obtained using the HF alkylation process, and sample 3 was obtained through the AlCl_3 process.

EXPERIMENTAL PROCEDURES

Solubility. The solubility of the different sulfonate solutions was determined by measuring the Krafft point, that is, the temperature at which a transparent sulfonate solution becomes cloudy on cooling.

Viscosity. Viscosity determinations were made at 30°C using a viscosimeter HAAKE RV 100 with a NV meter equipment (HAAKE Co., Karlsruhe, Germany).

Surface tension. The determination on this parameter was done with LAUDA MGW (Lauda-Königshofen, Germany) equipment. In principle, the instrument electronically measures the force which is applied by the liquid to an immersed measuring probe. In our case we have used the ring method. According to de Nouy: when taking the ring (Pt-Ir alloy, 6 cm circumference), a liquid lamella is pulled out of the liquid and the force is measured as a function of the length of the lamella.

Critical micelle concentration (CMC). This variable was based on the measurement of the specific electrolytic conductivity at different LAS concentrations. When the specific electrolytic conductivity is plotted against the LAS concentration, the curve obtained has a sharp break in it. The concentration at which this break occurs corresponds to the CMC.

The equipment used was a CRISON-522 (CRISON INSTRUMENTS, Barcelona, Spain) with a cell constant of 0.87 cm^{-1} . This equipment has a measurement range from 20 s to 200 s, and has the possibility of cell constant compensation either in $\text{s} \times \text{cm}^{-1}$ or $\text{ms} \times \text{cm}^{-1}$ for direct conductivity measurements.

As a calibration standard, we have used sodium dodecylsulphate and found a CMC of 8.5 mmol/L, whereas the value found in the literature (3) was 8.3.

Detergency performance. Detergency performance tests were carried out according to the ASTM-D-3050/75. Washing was carried out in the Terg-O-Tometer (U.S. Testing Co., Hoboken, NJ). Six test samples (artificially standard soiled cotton pieces) were placed in each jar with one liter of various hard water/detergent solutions. Washing was carried out at 30°C for 20 min.

Following washing, each swatch was rinsed with distilled water for 10 min at the same conditions as for washing and then air-dried.

Soil removal was measured by reading the reflectance of the standard cloths before and after the washing cycle. The instrument used was an XL-23 Colorimeter (GARDNER INSTRUMENTS, Bethesda, MD).

As the Terg-O-Tometer equipment uses six pieces of cloth per jar, the detergency results are an average of six values and the LSD (least significant difference)

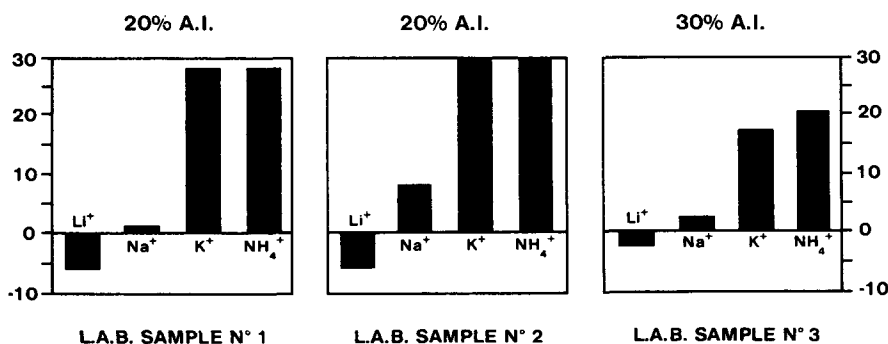


FIG. 1. LAS Krafft point vs counterions. Footnote to Figure 1: Sample 3 had to be tested at 30% active ingredient because of its much higher solubility as compared with the other two samples and with the aim of appreciating significant differences between the various counterions.

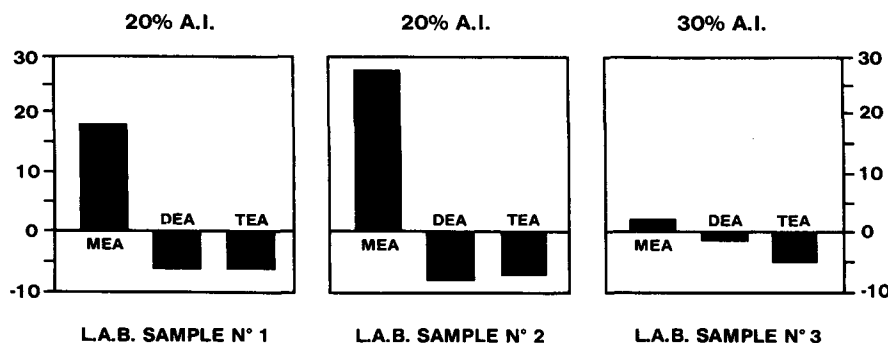


FIG. 2. LAS Krafft point vs counterions.

TABLE 2

Hydration Energy of Different Cations

	Hydrated radius (Å)	Hydration energy (kcal/mol)	Ionic radius (Å)
Li ⁺	3.40	124.4	0.60
Na ⁺	2.76	97	0.95
K ⁺	2.32	77	1.33
NH ₄ ⁺	1.88	72	1.48

between two experimental samples is one unit of reflectance increase, at a 95% confidence level.

RESULTS AND DISCUSSION

Solubility—inorganic ions. The experimental results are plotted in Figure 1. The larger the ionic radius of the counterion, the lower the solubility regardless the starting LAB used NH₄ < K < Na < Li (solubility increase). As expected, the increase in solubility has a direct relationship with the polarizing strength of the counterion and therefore with its hydration ease.

This is confirmed by the hydration energy, the hydrated radius of the different counterions and the well-known fact of the similarity between potassium and ammonium

salts, as indicated in Table 2 (4). When considering the hydrophobic part of the molecule, for a given counterion, the solubility decreases according to the following order: sample 3 > sample 1 > sample 2. However, these results are to be expected because of the high tetralin content (with a hydrotrope-like effect) of sample 3, and the difference in the molecular weight between samples 1 and 2 which have a similar tetralin content (5).

Solubility—organic salts. The results are shown in Figure 2. The more ethanol groups in the amine, the better the solubility, no matter the LAB used. Therefore, the solubility increases in this order: MEA < DEA < TEA, although no significant differences between DEA and TEA can be observed for 20% active ingredient (A.I.) solutions of sulfonates derived from samples 1 and 2. Concerning the hydrophobic part, the same conclusions as with the inorganic ions can be drawn, thus, for a given counterion the solubility decreases in this order: sample 3 > sample 1 > sample 2.

Viscosity—inorganic ions. Figure 3 shows the viscosity results which can be summarized as follows: Viscosity follows the opposite direction of solubility. The larger the counterion size, the more viscous the sulfonate solution: Li < Na < K < NH₄.

As far as the hydrophobic part is concerned, the three different alkylbenzene sulfonate solutions of a given counterion show a decreasing viscosity in the following order: sample 2 > sample 1 > sample 3. These results can

INFLUENCE OF STRUCTURE AND COUNTERIONS ON SULFONATES

INORGANIC COUNTER IONS — TEMP : 30° C

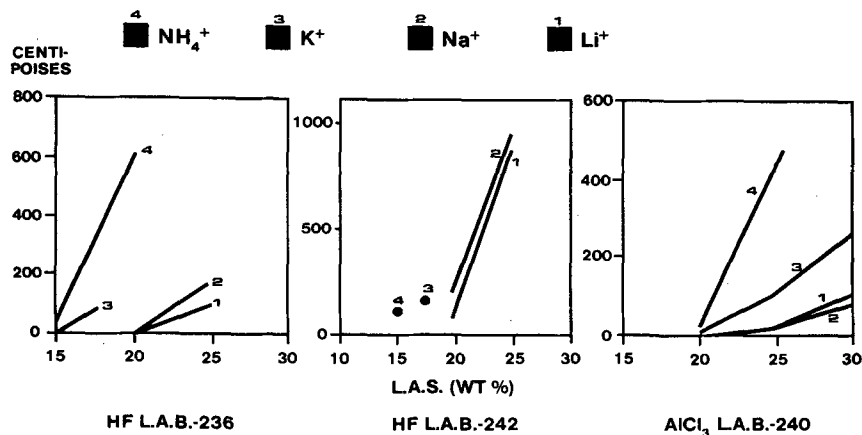


FIG. 3. Viscosity vs A.I. concentration.

ORGANIC COUNTERIONS — TEMP : 30° C

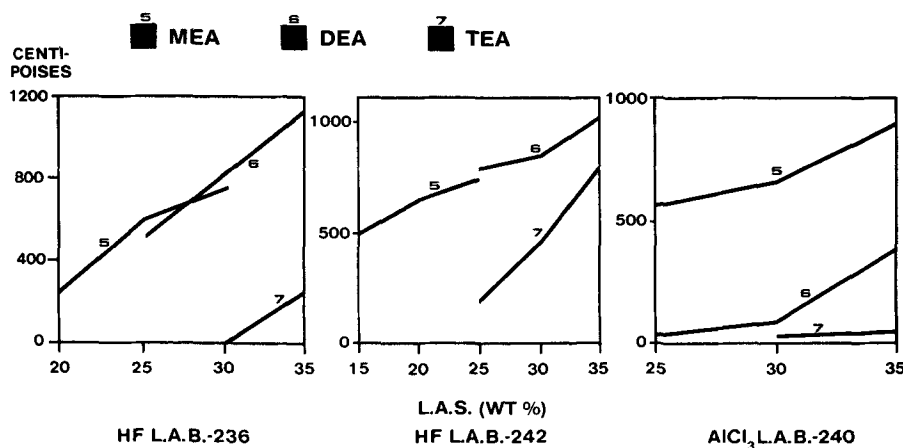


FIG. 4. Viscosity vs A.I. concentration.

be justified once more as a consequence of the tetralin content of alkylate 3 which acts as a viscosity depressor, and also because of the difference in the molecular weight between alkylate samples 1 and 2. Thus, the lower the molecular weight of a similar type of LAB (same tetralin content), the lower the viscosity and the better the solubility.

Viscosity—organic salts. (Fig. 4) The higher the number of ethanol groups in the molecule, the lower the viscosity. This reduction in viscosity is particularly noticed in sample 3. With respect to the hydrophobic part, viscosity decreases following the same order as in the case of the inorganic salts: sample 2 > sample 1 > sample 3.

Surface tension. Figures 5, 6 and 7 represent the surface tension vs surfactant concentration of the three samples used. The general mathematic equation for these graphs obtained by linear regression analysis is as follows: $y = -\log x + b$. The counterion influence on the surface tension was determined according to the parameters defined by Rosen (1), as efficiency and effectiveness, using the following criteria for the estimation of these parameters.

Efficiency is the surfactant concentration required to

lower solvent surface tension 20 dynes/cm. Effectiveness is the reduction of solvent surface tension attained at a surfactant concentration close to the CMC. The reduction of the surface tension beyond the CMC is relatively insignificant. As it can be observed in Table 3, no differences in effectiveness among the four counterions are noticed except for sample 1.

Concerning efficiency, according to Rosen: "surface tension reduction depends on the replacement of solvent molecules at the interface by surfactant molecules, thus the efficiency of a surfactant in reducing surface tension should reflect the concentration of the surfactant at the interface relative to that in the bulk liquid phase. The replacement of the counterion by one more tightly bound (ions with small hydrated radius e.g. K⁺, NH₄⁺) increases the efficiency, presumably by decreasing the net electrical charge on the surfactant molecule." As a consequence of this net electrical charge reduction, the electrical repulsion between anions already adsorbed and those reaching the interface decreases, thus allowing more surfactant molecules to concentrate at the surface, and therefore, resulting in a significant efficiency increase.

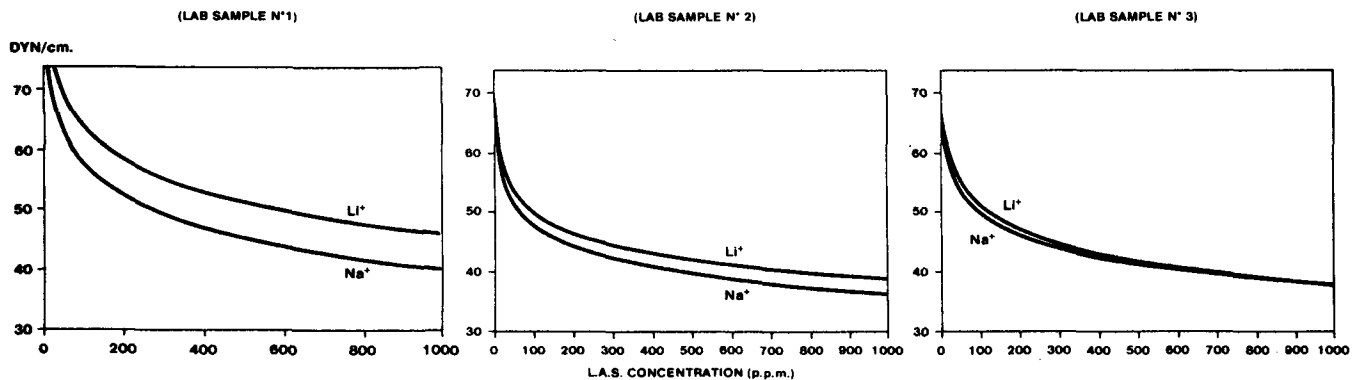


FIG. 5. Surface tension vs concentration.

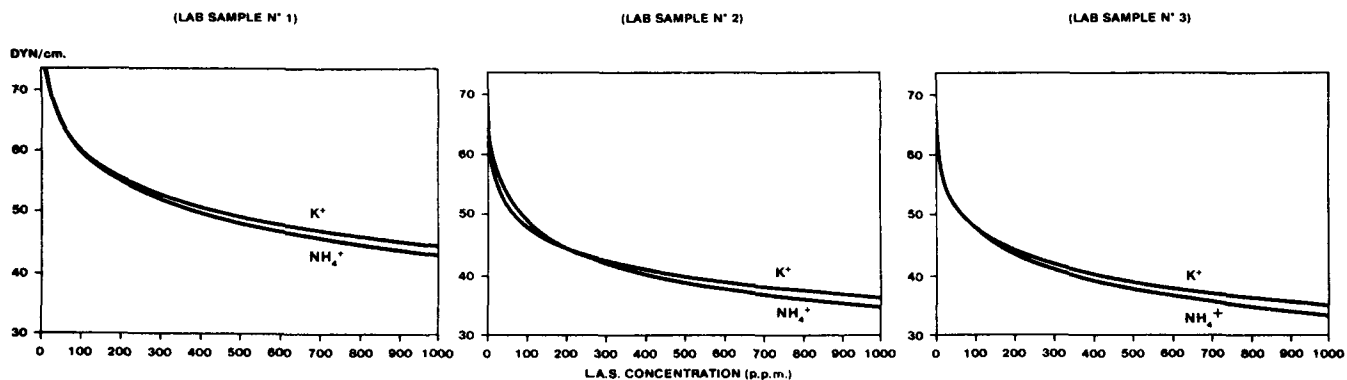


FIG. 6. Surface tension vs concentration.

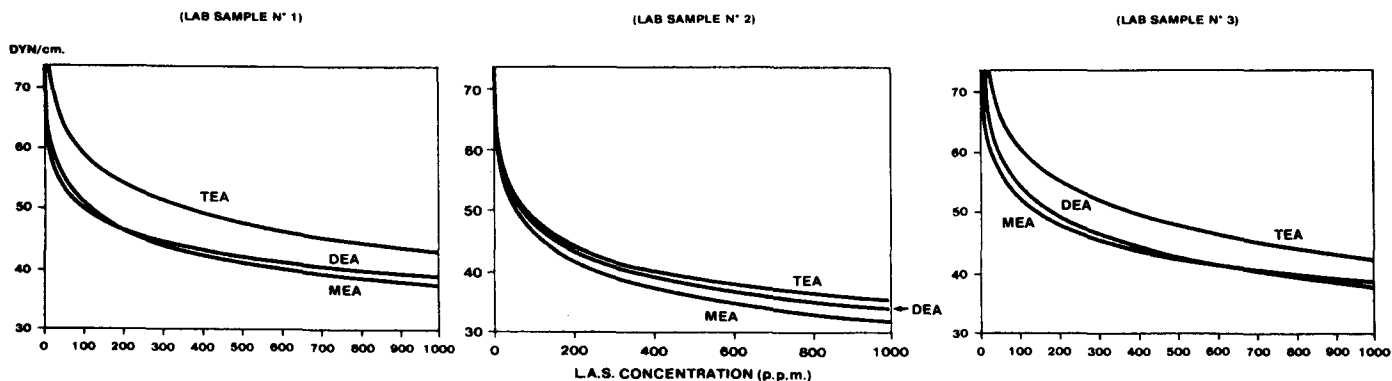


FIG. 7. Surface tension vs concentration.

TABLE 3

Surface Tension of Inorganic Sulfonates

	Sample 1				Samples 2 and 3			
	Li ⁺	Na ⁺	K ⁺	NH ₄ ⁺	Li ⁺	Na ⁺	K ⁺	NH ₄ ⁺
Efficiency (ppm of surfactant)	500	250	280	300	62.5	62.5	62.5	62.5
Effectiveness (dynes/cm)	47	41	41	41	37	37	35	36

INFLUENCE OF STRUCTURE AND COUNTERIONS ON SULFONATES

L.A.S. - INORGANIC COUNTERIONS (L.A.S. SAMPLE 2)

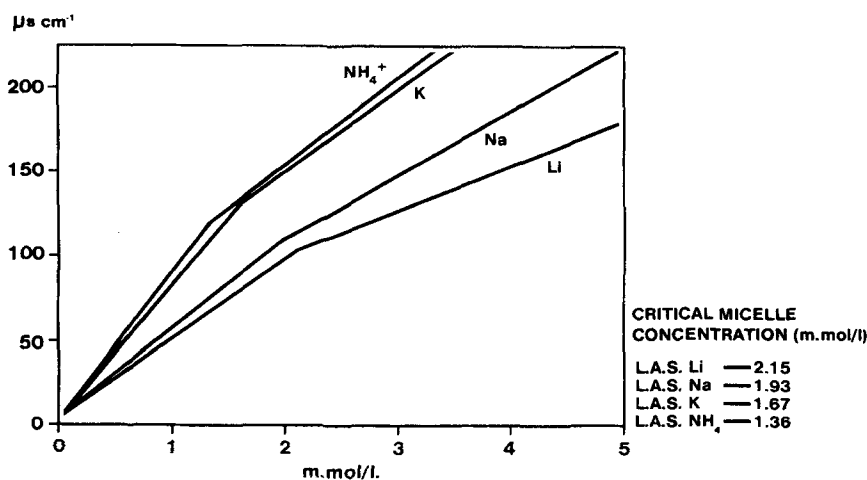


FIG. 8. Specific conductivity vs concentration.

L.A.S. - ORGANIC COUNTERIONS (L.A.B. SAMPLE 2)

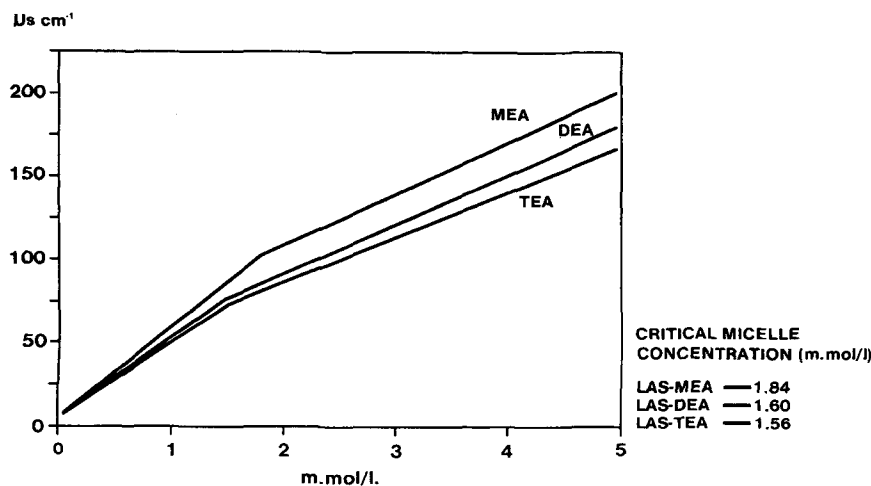


FIG. 9. Specific conductivity vs concentration.

Concerning effectiveness, and due to similar reasons, the anions associated with counterions of the lowest hydration radius are more effectively adsorbed, although in this case the effect due to the counterion is less significant. Among the sulfonates considered in this work, the above theory can only be confirmed with the Li⁺ salt derived from the lowest molecular weight alkylbenzene (sample 1). For a given counterion, there are significant differences between sample 1 and the other samples. The superior performance of samples 2 and 3 compared to sample 1 is justified with an increase of the surface activity, due to the longer alkyl chain of samples 2 and 3.

Surface tension—organic salts. The best results are always obtained with MEA and DEA regardless of the starting alkylbenzene used: MEA = DEA > TEA. These results are in agreement with the conclusions already obtained with the inorganic counterions. In the case of TEA,

others factors such as the steric hindrance and the hydrogen bonds alcohol-solvent will justify its particular behavior.

Critical micelle concentration (CMC)—inorganic ions. The results are plotted in Figure 8, and it can be appreciated that CMC decreases in the following order: Li > Na > K > NH₄. These results are in good agreement with other authors (1) and they can be explained because CMC reflects the counterion micelle degree of binding. Therefore, in aqueous systems, an increased binding of the counterion causes a decrease in the CMC of the surfactant. The bigger the counterion hydration radius, the weaker the counterion micelle degree of binding. This is a logical conclusion, because an increase in counterion hydration radius means an increase in the distance to the micelle and therefore a reduction in the degree of binding.

CMC—organic salts. (Fig. 9) CMC results can also be

TABLE 4

Detergency Performance (R)

Counterion	Active ingredient use level (wt%)				
	0.15	0.6	1.5		
	Water hardness (ppm as CaCO ₃)				
	150	150	300	150	300
	ΔR				
Li ⁺	25.8	38.2	38.1	36.8	36.7
Na ⁺	25.3	38.6	37.7	37.2	36.7
K ⁺	24.6	37.8	37.6	36.1	37.6
NH ₄ ⁺	25.8	37.6	37.6	36.0	37.5
MEA	25.8	37.7	36.2	37.3	38.6
DEA	24.8	36.6	35.6	37.2	36.5
TEA	24.4	36.8	34.6	35.4	36.3

TABLE 5

Detergency Performance

ΔR of pure LAS vs EMPA-101

Counterion	ΔR
Li ⁺	28.8
Na ⁺	29.7
K ⁺	29.0
NH ₄ ⁺	29.5
MEA	29.4
DEA	29.8
TEA	28.5

explained using the same arguments as with the inorganic ions. In addition, there are other factors which will justify

the particular behavior of the amine derivatives. These factors are: the formation of hydrogen bonds alcohol-water, steric hindrance and the influence of the OH group. The general trend of the CMC was: MEA>DEA>TEA.

Detergency performance. Detergency performance tests were carried out under the following conditions: equipment: Terg-O-Tometer; reflectometer: Gardner XL-23; fabric: EMPA-101 (cotton); temperature: 30°C; water hardness: 150, 300 ppm (as CaCO₃); formulation: LAS: 20% STPP: 30%; and LAS used: sample 2.

The reflectance increase data are summarized in Table 4.

In order to avoid the builder's influence as well as water hardness effect, another experiment was conducted to reflect the behavior of the surfactant alone. The parameters used in this experiment were: fabric: EMPA 101; temperature: 30°C; water hardness: 0 ppm as CaCO₃; surfactant used: LAS derived from sample 2; and use level: 0.6%.

The corresponding R values are indicated in Table 5, where no significant differences can be appreciated among the various counterions used.

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